

# Experimental aspects of temperature-modulated dilatometry of polymers

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## Abstract

Polymers are materials marked by specific physical properties, different from those such as metals, alloys or ceramics. Temperature-modulated temperature profile in the investigation of polymers by dilatometry may have many outstanding features, similar to those of temperature modulated DSC. However the experimental conditions are more stringent than those of conventional dilatometry. An overview of dilatometer types is presented. Taking into account specific properties of the sample such as softness and heat transfer, an optimal choice of dilatometer was made and experimental conditions were established.

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## 1. Introduction

Thermal expansion measurements and the determinations of softening temperature provide important information in polymer science, which can be correlated with those obtained by differential scanning calorimetry (DSC). Thermal expansion can be obtained by microscopic and macroscopic analysis. In the first case, the lattice parameters are determined by the X-ray diffraction (XRD) [1], the latter case, information is obtained from volume change [2]. The changes of volume involve changes in dimensions, since for practical reasons, linear dilatometers are most widely used. The changes in length of the sample can be measured in several ways, e.g. by laser beam or mechanically by transducers. Mechanical types involve families of instruments applied in the thermomechanical analysis (TMA) and dilatometry (DIL). Both techniques monitor the change in volume or corresponding length with temperature under controlled or negligible low mechanical load. Since the introduction of temperature-modulated DSC [3], a variety of temperature-modulated (TM) programs have been developed with outstanding features in thermogravimetry (TMG) [4] and thermomechanical analysis (TMA) [5,6]. As reported earlier [7], the TM-TMA experiment involves an experimental error

in temperature mainly due to the heat transfer. The calibration procedure was developed and applied [8].

In this article, we discuss the experimental aspects of temperature-modulated dilatometry of polymers considering different construction of push-rod dilatometers. The described observations were made during an experiment demonstrating the frequency dependence of thermal expansion of polystyrene in the region of the glass transition [9].

## 2. Experimental

### 2.1. Overview of dilatometer types

#### 2.1.1. Configuration

There are two configurations that are used, depending on the experimental requirements. One is the horizontal configuration with the sample lying in a dilatometer tube. This position is suitable for the measurement of a thin rod. This shape ensures a low temperature gradient within the sample when the temperature program provides a fast heating rate. The push-rod is attached to one end of the sample and tracking pressure results from application of a linear variable displacement transducer (LVDT).

In the vertical configuration, the sample stands on the plate-end of the dilatometer tube with the push-rod resting on it. Tracking pressure can be reduced, but not below a minimum required for smooth and continuous movement.

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Thermal uniformity is inferior in comparison to a horizontal instrument.

### 2.1.2. Heating type

Depending on the sample material, the temperature range and the heating rate, the heat to the specimen can be transferred in different manners: electrical induction, thermal conduction, convection and/or radiation.

The inductive type can be applied to the electrically conductive materials only, so the method is not applicable to polymers.

In the direct conductive method, the sample is in thermal contact with the furnace block. An advantage is good temperature uniformity with fast heat up.

In the convection type dilatometers, nickel–chromium wire heaters are coiled on a ceramic tube. In this case, the region surrounding the sample is heated, rather than the sample itself. The temperature sensor is kept between the furnace and sample. This method is relatively slow.

In IR radiant heating, a sample is placed in the focus of thermal radiation. The temperature sensor is attached to one end of the sample and has good thermal contact with the specimen but it also is exposed to thermal radiation. This type provides very fast heating and enough fast cooling when purge gas is used. A temperature program with modulation can be applied.

### 2.1.3. Temperature sensor

In most construction of the dilatometers, thermocouples are used, except for the ultra-high temperature measuring systems that employ pyrometers. Depending on the temperature range, different types of thermocouples are applied for temperature control and measurement. The most important problem in dilatometric investigation is the sample temperature determination when the temperature is modulated.

### 2.1.4. Dilatation sensors

At present, the linear variable displacement transducers (LVDT) are widely applied to measure sample elongation in push-rod dilatometers. This type of displacement sensor ensures

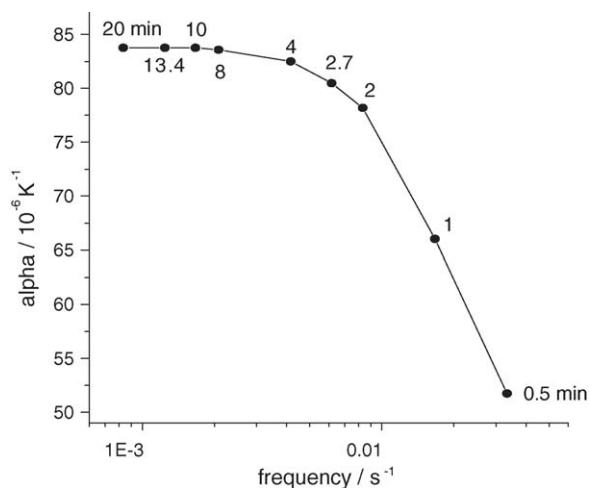


Fig. 1. CTE ( $\alpha$ ) of polystyrene obtained from amplitudes of the sample temperature,  $A_{T_s}$ , and dilatation,  $A_{DIL}$ , in the frequency range from 0.0003 to 0.04 Hz at the temperature of 95 °C.

the resolution of 10 nm. In case of soft materials such as polymers at certain temperatures, the push-rod tends to indent into the sample. The maximal reduction of tracking pressure is necessary but it results in jerky movement when very low force is used. The appearance of the effect becomes significant when the length of the sample follows small changes of temperature.

Summarizing what was mentioned above, authors applied push-rod dilatometer with radiant heating for the dilatometric investigation of polymers with linear temperature program superimposed with a modulation. The experiment was carried out with a sample in the shape of a rod 30 mm in length and 3 mm in diameter. Dilatation was recorded in a differential mode with a quartz sample as reference. Temperature-modulated profile by IR radiant heating was applied. To obtain reasonable quantitative results, the experiment had to be modified by considering the heat transfer to the sample and its temperature, ratcheting movement of the dilatometer due to very low tracking force applied, and small sample length oscillations resulting in effect similar to hysteresis one. The coefficient of thermal expansion (CTE)— $\alpha$ —is calculated from the amplitudes of the modulated temperature,  $A_{T_s}$ , and the corresponding dilatation,  $A_{DIL}$ , is obtained as a ratio  $A_{DIL}/(A_{T_s} L_0)$ , where  $L_0$  is the initial length of the sample.

## 2.2. Temperature and heating

We have experimentally found that the temperature of the sample distinguishes from the measured one by the thermocou-

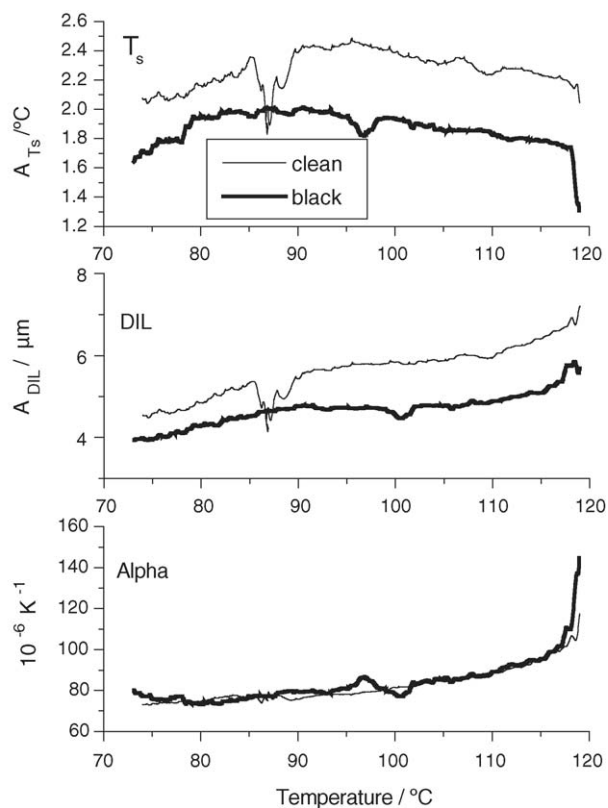


Fig. 2. Effect of coating the sample with a black paint. The amplitude,  $A_{T_s}$ , for the clean sample is higher than for black surface. The state of the surface does not influence the result of  $\alpha$  coefficient.

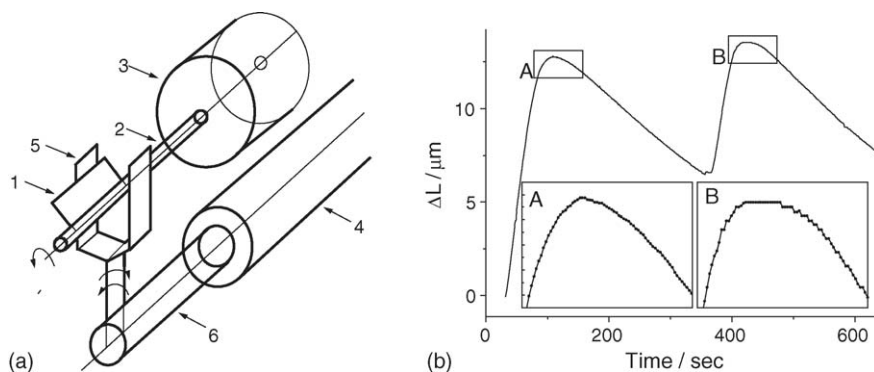


Fig. 3. Mechanical improvement of LVDT movement by vibrating push-rod (a): (3), electric micro motor; (2), rotor with frame (1); (5), spring; (4), LVDT; (6), measuring spindle. Dilatometric signal recorded during two thermal pulses with vibrator (b): switched-on at region (A) and switched-off at region (B).

ple when temperature is modulated. In the case of low frequency, the investigated system is in thermal equilibrium. If the sample is free from any transition, the elongation and shrinkage will follow the temperature and the obtained CTE is frequency independent. This is illustrated in Fig. 1. The values of CTE are the same for the periods: 20, 13.4 and 10 min. Starting from a certain frequency (periods between 10 and 8 min) one can see, that the CTE has a tendency to decrease with increasing frequency. This experimental fact demonstrates that with increasing frequency, the measured temperature does not correspond to the true sample temperature. Considering the thermal path between the sample, thermocouple and heating source, a temperature correction algorithm for higher frequency was developed and is described in [10]. Furthermore, the temperature-modulated experiment is considered in the low frequency range only for simplicity.

Samples (one under investigation and a second one as reference) are exposed to the IR radiation from three halogen lamps (1 kW each). Parabolic aluminum mirrors focus the radiation at the surface of the samples. Thermal response of a specimen exposed to modulated heat depends on several factors considered by many authors [11]. In case of radiant heat, absorption/radiation properties of the surface play a significant role. Blackbody surface is the best defined and blacking is used usually in such experiments. In order to establish this influence, two measurements were performed: one with clean and one with black surface of the polystyrene sample in the frequency range where CTE is frequency independent. The result is illustrated in Fig. 2. The amplitude of the sample temperature,  $A_{T_s}$ , and the corresponding amplitude of dilatation,  $A_{DIL}$ , are depicted for two cases: clean sample as obtained (thin line) and a black sample (thick line). One can see how the state of the surface influences the sample temperature. The observed effect is opposite to that expected: an uncovered, clean sample has a higher temperature than a black one. The fact can be explained by considering IR spectrum of polystyrene, which has absorption around  $3.2 \mu\text{m}$  wavelength of IR radiation. However, the state of the surface doesn't influence the obtained result of the coefficient of thermal expansion—alpha. At about  $85^\circ\text{C}$  an unintentional effect due to instability of the temperature is also seen which affects the dilatation but not the value of the alpha coefficient. Some other artifacts originate most probably from mechanical defor-

mation of the sample–thermocouple system during heating and have no physical meaning.

### 2.3. Dilatation

The type of displacement sensor was chosen with minimal tracking force from among those commercial available. BROWN & SHARPE TESA SA type was chosen which has a tracking force from 0.3 to 0.6 N. Besides being a high performance sensor of this type, the application to soft materials results in delayed movement and limited accuracy, as it is illustrated in the insert B of Fig. 3b. The sensor does not follow the dilatation smoothly and has 'dead zone' where it is not sensitive to small changes of length.

Significant reduction of such jerky movement and improved sensitivity of the dilatometer was achieved by vibrating the moving part of the LVDT as illustrated in Fig. 3a. The frame (1) is attached to the rotor (2) of small electric motor (3), placed along the LVDT (4). The frame rotates inside a split of a spring

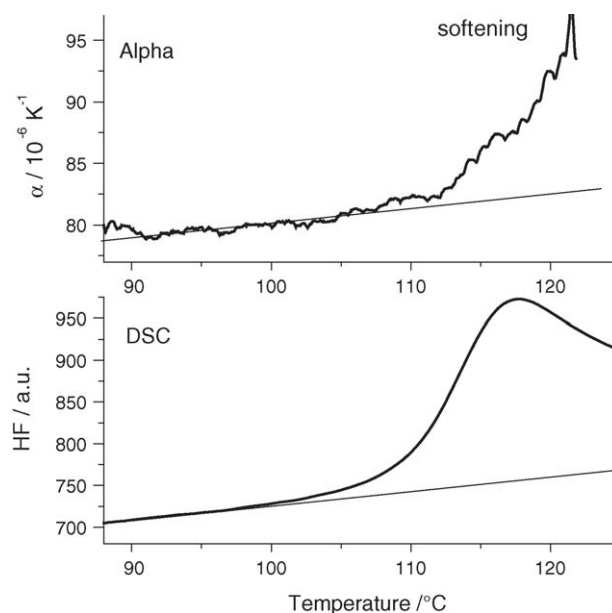


Fig. 4. CTE (alpha) behavior of polystyrene as a function of temperature by temperature-modulated program in the range of glass transition in comparison with result from DSC.

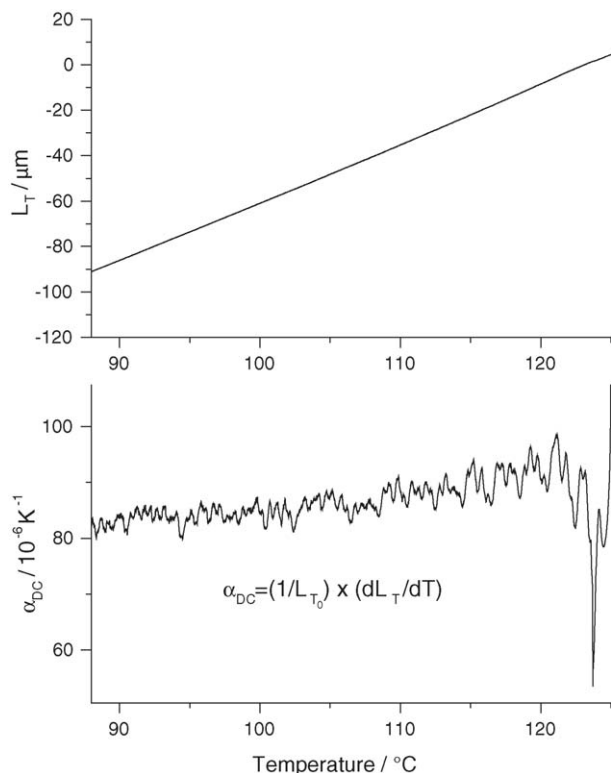


Fig. 5. Length changes of the sample in a function of temperature (upper window) and corresponding coefficient,  $\alpha_{DC}$ , calculated from instantaneous changes  $dL_T/dT$  (lower window).

(5) attached to the end of measuring spindle (6) of the LVTD. The rotating frame cyclically pushes from one to other side of the spring transferring movement to the spindle. The rod cannot rotate but moves slightly allowed by a small mechanical looseness. This movement is sufficient to reduce static friction enabling smooth longitudinal shift of the spindle of the LVDT.

This effect is illustrated in Fig. 3b. For comparison, the dilatation response of the sample on two thermal pulses is shown. The critical region is when the elongation of the sample changes into the shrinking (or opposite). These regions are magnified at the bottom of the figure. The vibrator was switched-on during first cycle (A), and then switched-off during second cycle (B). Jerky movement of the dilatometer is noticed when the vibrator is switched-off. This effect can cause an error of the dilatometric measurement higher than 30% for small amplitudes.

### 3. Results

Taking into account precautions described above, we have measured the CTE of polystyrene as a function of temperature using a temperature-modulated program. A sample was not coated; it was used as obtained from pressing form. An annealing procedure was applied before the measurement. The frequency range was chosen as low as possible (period 10 min) to compromise with reasonably short measuring time. As we have found, this frequency system is yet in a quasi-equilibrium state. The heating rate was  $\langle q \rangle = 0.25 \text{ K/min}$ , and the programmed temperature amplitude  $A_T = 1.5 \text{ }^\circ\text{C}$ . The result is illustrated in Fig. 4,

with comparison to the DSC trace. The CTE for polystyrene below the glass transition was obtained as  $85 \times 10^{-6} \text{ K}^{-1}$ . Starting from a temperature of  $110 \text{ }^\circ\text{C}$ , the CTE increases up to a maximal value of  $97 \times 10^{-6} \text{ K}^{-1}$  at  $123 \text{ }^\circ\text{C}$ . At this temperature, a softening is observed and further measurement is not possible. This behavior of CTE has the same character as changes in heat capacity observed by conventional DSC (lower trace in Fig. 4). The result is obtained for a sample with the same thermal history, except heating rate, which was  $20 \text{ K/min}$ . To provide exact experimental correspondence, a temperature-modulated DSC would be worthwhile to apply.

### 4. Conclusions

A temperature-modulated method in dilatometry enables the measurement of the instantaneous coefficient of thermal expansion in a narrow temperature range with higher sensitivity as opposed to the conventional DC method. The conventional dilatation and it is unavoidable in such a type of instrument [12]. For comparison, the result obtained for DC components is illustrated in Fig. 5. The value of  $\alpha_{DC}(T)$  exhibits a large scatter masking the true dilatometric effects.

Frequency of the modulated temperature is limited to the low frequency range where the system is in equilibrium. Softness of the polymeric materials requires as low tracking pressure as possible, so small vibrations of moving spindle of the dilatometer improves smooth movement and the resolution is enhanced. The state of the surface plays a role on heat transfer but does not have a significant influence on result of alpha coefficient measurement.

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